Photocatalytic degradation of fungicide difenoconazole via photo-Fenton process using α-Fe_2O_3

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Abstract

Nowadays, Human consumption leads to massive industrial sector manufacturing. Pesticides are one of the most toxic chemicals widely used to increase agricultural production. Those compounds present several threats to the environment. The photodegradation of difenoconazole (DFL) fungicide was carried out via Photo-Fenton process using synthesized α-Fe_2O_3 nanoparticles. The α-Fe_2O_3 was prepared using hydrothermal approach at 180°C with ferric chloride and sodium hydroxide reagents. The sample was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and Raman analysis. Average crystallite size has been recorded to be 27nm and the surface area was found to be S_{Bet}=24.82 m²/g. DFL removal has been tested under divers systems: UV photolysis, UV/H_2O_2, UV/α-Fe_2O_3, Fenton and Photo-Fenton process. The kinetic has been been monitored using High-Performance Liquid Chromatography (HPLC). All irradiation tests were achieved at 254 nm using UVC Lamp. An optimization of reaction conditions (pH, oxidant concentration, and catalyst dosage) were performed As a result, it was demonstrated that Photo-Fenton process (UV/ α-Fe_2O_3/H_2O_2) as most effective for DFL removal. The optimal catalyst dose of α-Fe_2O_3 for high removal rate is about 0.5g/l at initial solution pH. The mineralization efficiency attained 83.67%. The oxidation kinetics of DFL was recorded to accord with the pseudo-first order kinetic model. Finally, a possible mechanism pathway was proposed based on detected intermediates using gas chromatography-mass spectrometry (GC-MS) analysis.

Introduction

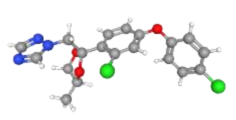
Over the last decade, the world's priority was to meet human food needs. Pesticides are chemical compounds created to deal with phytopathology for human survival exigency. They are classified depending on their principal target and chemical structure[1]. Insecticides, herbicides, fungicides, and nematicides are a broad array of products utilized every day in crop fields worldwide. Certainly, the agricultural production has been guaranteed, but in return, the treatment rate with those compounds exceeded the threshold to the contamination stage. Since the world has become more environmentally conscious, the governments have been oriented towards enormous investments in green technologies. The conventional processes of wastewater treatments represented in the Physico-chemical and biological techniques are still ineffective in removing persistent pollutants[6]. Therefore, a vigorous attempt has been made to find new clean alternative processes that are economic, widespread, renewable and have no impact on environment[7]. Advanced oxidation processes (AOPs) have been confirmed as promising technologies[8].

In the present work, we reported the synthesis of α-Fe_2O_3 nanoparticles with the hydrothermal method at 180°C. it manifested as an eco-friendly and economical approach with low-cost reagents and a simple fabrication method. The sample properties were characterized using a range of analytical technique XRD, SEM, TEM, and RAMAN analysis. The potential photocatalytic activity of α-Fe_2O_3 nanoparticles under UV light source was investigated by monitoring the degradation of difenoconazole (DFL) Table1, a fungicide of dioxolane class, widely used for fruit, vegetables, and cereals disease control. It considered a toxic product in an exceeded dose; a deterioration of environment and human health is expected in long term used. A possible photocatalytic mechanism pathway was proposed to elucidate the enhancement of DFL photodegradation.

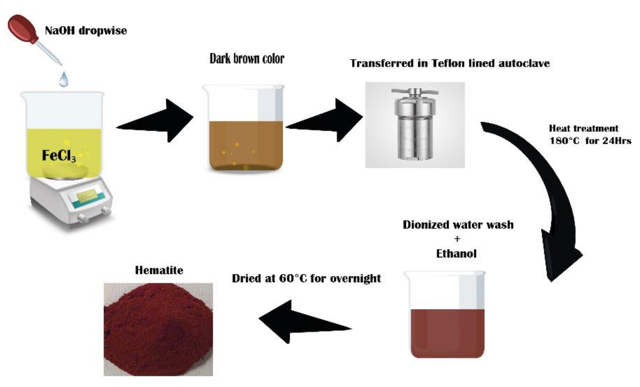
Materials & Methods

- **Substrate :**

Definoconazole (fungicide)



- **Synthesis protocol of α-Fe_2O_3 :**



- **Characterization of synthesized α-Fe_2O_3**

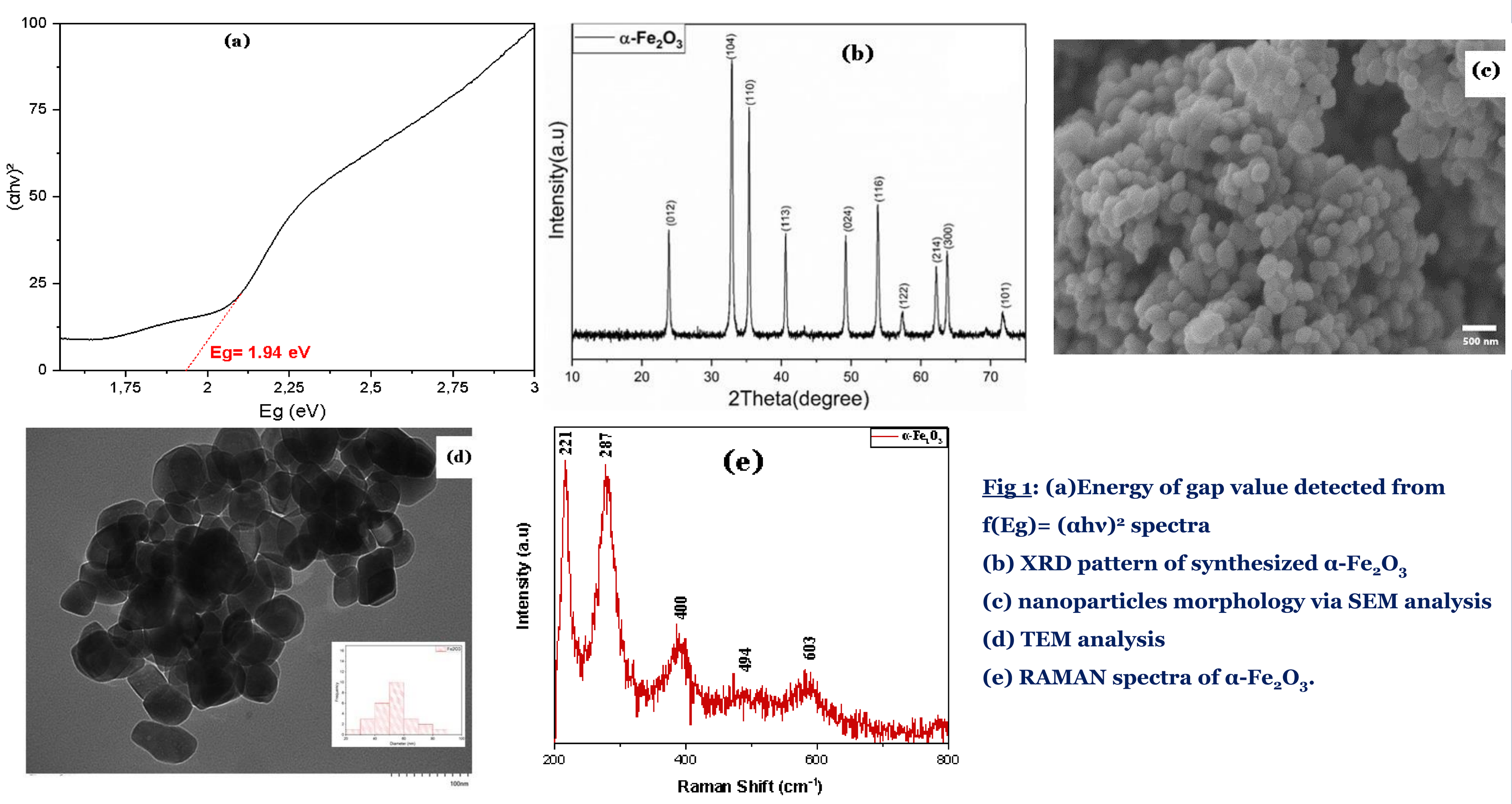


Fig 1: (a)Energy of gap value detected from f(Eg)= (αhν)² spectra
(b) XRD pattern of synthesized α-Fe_2O_3
(c) nanoparticles morphology via SEM analysis
(d) TEM analysis
(e) RAMAN spectra of α-Fe_2O_3.

The optical properties of the synthesized photocatalyst: the sample Bandgap has been recorded using the Tauc equation, the specific surface area of the photocatalyst S_{BET} = 24.82 m²/g. The XRD spectra shows a strong pure phase. The sample composed of crystals with semi-spherical shape. The grain size of the monodisperse nanoparticules is about 52nm.

Results & Discussion

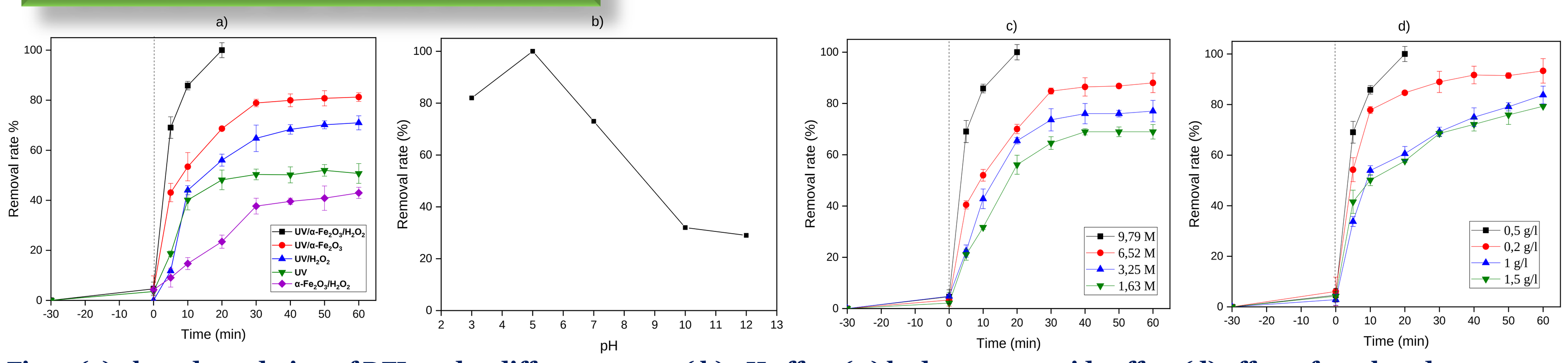
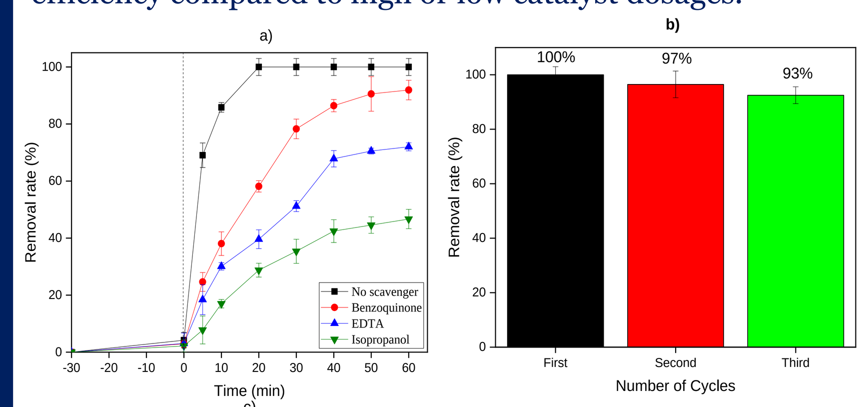


Fig.2: (a) photodegradation of DFL under different system(b) pH effect (c) hydrogen peroxide effect (d) effect of catalyst dosage.

In the beginning, DFL photodegradation was performed under different systems: direct photolysis, UV/H_2O_2, UV/α-Fe_2O_3, Fenton and Photo-Fenton process. As shown, in Fig.4a, Photo-Fenton process was observed to be the most effective over other methods, achieving a total removal 100% within 20 min. the optimum pH that manifested an effective treatment was pH=5. Hence, the impact of H_2O_2 concentration was carried out and 9,79M was found the ideal concentration for Photo-Fenton reaction. 0.5 g/L of catalyst improves an important efficiency compared to high or low catalyst dosages.



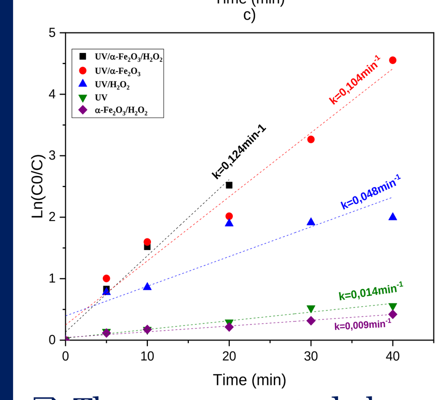


Fig.3:
(a) scavengers study
(b) reusability of catalyst
(c) kinetic study Ln(C_0/C)=f(time)

- The scavenger study has maintained with the commonly used quenchers, isopropanol, EDTA, and benzoquinone as a captive of OH˙, h⁺, and ˙O_2 radicals, respectively. with the addition of isopropanol, the removal rate reported a substantial decrease of 52% . Hence, both species h⁺, OH˙ were found to be the responsible radicals in difenoconazole photodegradation process.
- The decrease of catalyst efficiency after several uses was explained by the loss of chemical stability of material induced by the photocorrosion phenomenon.
- the photocatalytic degradation processes followed the pseudo-first-order kinetics.

Mechanism & Mineralization

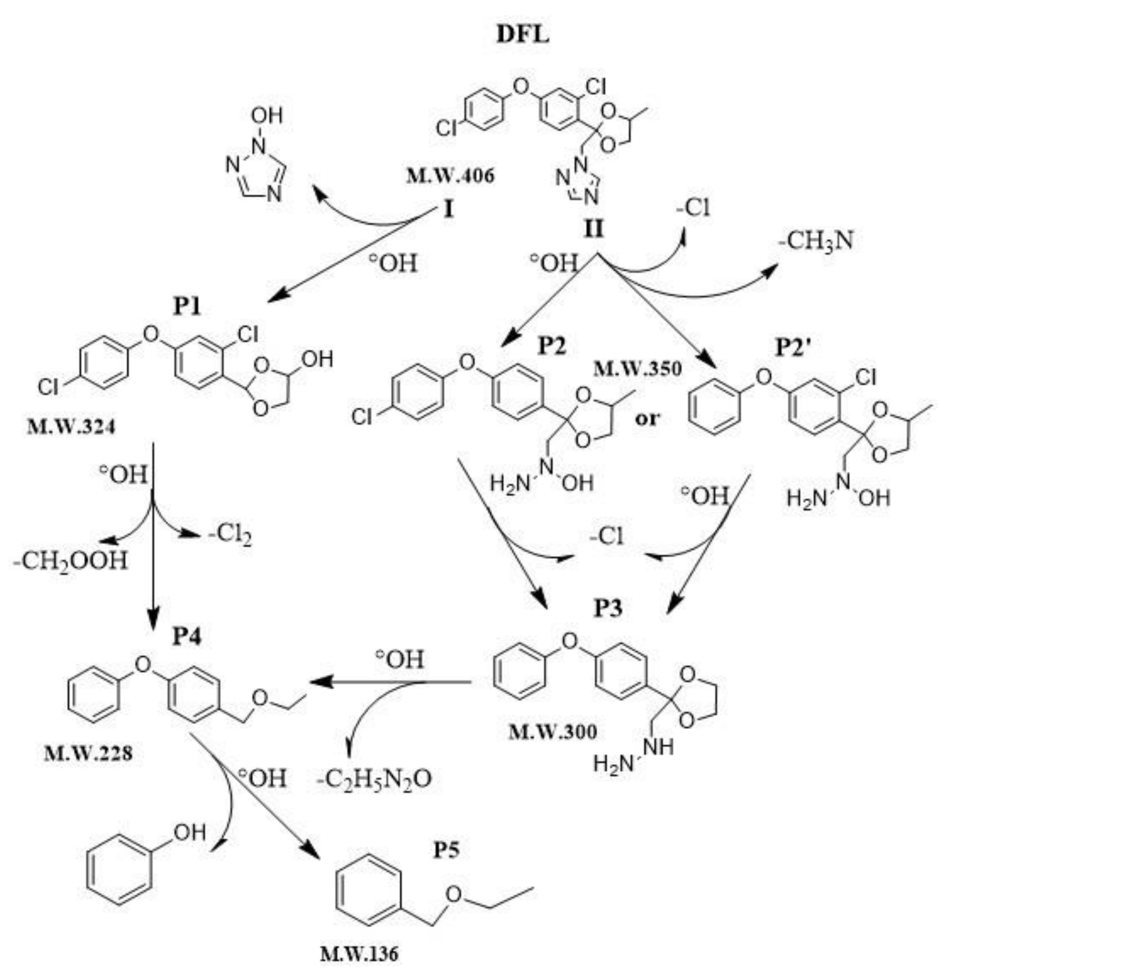


Fig.4: Proposed transformation pathway

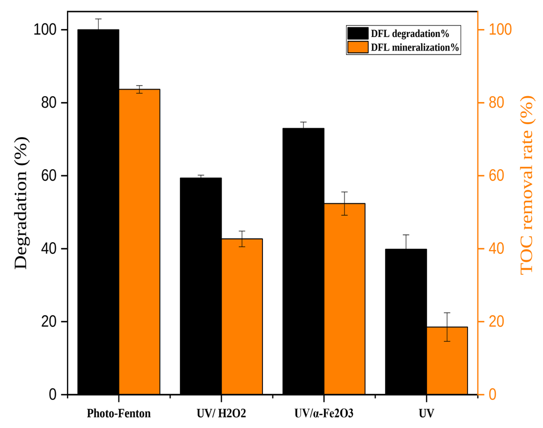


Fig.5: Degradation and TOC removal rate

- The samples were extracted in dichloromethane solution after 60 min of photocatalytic reaction. The intermediates were followed using gas chromatography coupled with mass spectrometry (GC-MS) analysis system.
- At 60 min, it has been found that UV photolysis, UV/catalyst and UV/H_2O_2 mineralized 18.53%, 52.37% and 42.69% respectively. Otherwise, the combined process UV/ α-Fe_2O_3/H_2O_2 detected to be the highest TOC removal rate of 83.67%.

Conclusion

Micropollutants were the aim of many research studies since the environmental and health contamination alert. Innovative technologies were established to deal with the wastewater treatment. Our study was focused on heterogeneous photocatalysis process. A hydrothermal process was used to synthesis α-Fe_2O_3,an abundant and low-cost naturel and synthesized metal oxide . The result sample has been characterized in detail wih XRD, TEM, SEM, and RAMAN spectra to detect its physic-chemical material properties. The Photocatalytic activity of powder was tested on a widely used fungicide, Difenoconazole that targeted as a toxic compound in overdoses. A duplicated series of experiments under different systems have been realized as a way to investigate the practical process for photodegradation of pollutant. The Photo-Fenton-like process has been proven a high efficiency among all tested methods with a high removal rate detection in only 20 min of treatment. Hence, the conditions of different parameters of Photo-Fenton reaction were optimized. The hydroxyl radicals are found to be responsible for the photodegradation reaction as a result of reaction scavengers study.

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